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Quasi-Amorphous Colloidal Structures for Electrically Tunable Full-Color Photonic Pixels with Angle-Independency

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Colloidal particles have been widely employed in materials science as templates for creating functional materials, model systems for investigating intrinsic forces in self-assembly, and phase transition behaviors of materials.[1–5] In particular, self-assembly of dielectric colloidal nanoparticles has often been applied for fabricating photonic band gap (PBG) materials.[6–8] Similar to other PBG materials prepared by self-assembly of block copolymers or by lithographic techniques, colloidal photonic crystals require crystalline or highly ordered periodic structures to exhibit PBG by the collective refraction in long-range.[9–11] In this case, the PBG can be tuned by modulation of periodicity or/and refractive index contrast.[9,12] While such tunable photonic crystals based on crystalline structures have recently been proposed as active components of display[13–16] and sensory devices,[12] their practical applications have been hindered by the intrinsic strong angle dependent hue of the crystalline PBG materials.

Recently, materials without long-range spatial order have also been investigated as a different class of PBG materials. In particular, "quasi-amorphous photonic materials", the colloidal structures with only short-range order on length scales comparable to optical wavelengths but without lattice periodicity or long-range order, exhibit spectral gaps dependent on the average particle distance.[17–21] Unlike typical crystalline photonic materials, quasi-amorphous structures show characteristic angle-independent and non-brilliant photonic color due to the coherent scattering of light from the isotropic nanostructures with short-range order.[17,20] In this case, the average inter-particle distance plays an important role to determine the position of PBG in quasi-amorphous materials. Similar structural colors were observed in particular animals and insects due to the presence of quasi-amorphous dermal protein arrays.[22–24] Despite their apparent technological importance and scientific interest, chemically[20] or electrically tunable quasi-amorphous photonic materials have barely been developed.

Herein, we report on the electrically tunable fast full color photonic display pixels exhibiting angle-independent photonic colors. Our approach takes advantage of the electrophoretically induced phase transition of colloidal nanoparticles from random fluid to quasi-amorphous structures, and their characteristic angle-independent optical properties. Fluidic colloidal nanoparticles can be deposited or concentrated on electrodes by applying electric field.[25–27] While crystallization is preferential for typical monodisperse colloidal particles, it can be suppressed to form quasi-amorphous structures when the polydispersity of particles is moderately high ($\delta > \sim 7\%$) and/or the particle concentration is above the critical concentration.[2,28] In this case, the quasi-amorphous colloidal structures exhibit photonic colors when the average inter-particle distance is in the length scale of the incident wavelengths, which can be further modulated by electrophoretic control of the local concentration of particles.

To test our idea, Fe_3O_4@SiO_2 core-shell nanoparticles were used as a model system. Superparamagnetic nanoparticles have been extensively investigated due to their unique magnetic properties, and recently used for magnetochromic materials.[29–31] In our experiments, however, Fe_3O_4@SiO_2 core-shell nanoparticles were chosen because of their high electrophoretic mobility in organic solvents and high optical contrast, not because of their magnetic properties. It was reported that incorporation of conductive materials within silica nanoparticles significantly enhanced the colloidal stability and the electrophoretic mobility, compared to pure SiO_2.[32,33] Furthermore, deep black color of Fe_3O_4 is desirable for enhancing optical contrast.

Fe_3O_4@SiO_2 core-shell nanoparticles were synthesized as previously described.[30,31] Briefly, Fe_3O_4 nanoparticle clusters were first synthesized by hydrolysis of iron(III) chloride in a basic condition at an elevated temperature (220 °C). Then, SiO_2 shells were formed around the Fe_3O_4 nanoparticle clusters through sol-gel process using tetraethoxysilane (TEOS) as a precursor for the formation of SiO_2. Finally

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DOI: 10.1002/adma.201001954

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Fe_3O_4@SiO_2 core-shell nanoparticles were collected by magnetic separation, and washed with ample amount of ethanol. Transmission electron microscopy (TEM) images confirmed that the core consists of many small Fe_3O_4 nanoparticles (d = ~10 nm), and the uniform SiO_2 shell formed around the core (Figure S1). The diameter of Fe_3O_4@SiO_2 nanoparticles was optimized to be 150 nm for our experiments. To suppress the crystallization, the polydispersity of the particles was intentionally controlled to be moderately high (δ_{core} = 14%, $\delta_{core+shell}$ = 9%). The purified Fe_3O_4@SiO_2 nanoparticles can be redispersed with high concentration in various polar solvents including water, methanol, ethanol, isopropyl alcohol, acetonitrile, dimethylformamide, dimethyl sulfoxide and propylene carbonate without further surface modification. Zeta potential of Fe_3O_4@SiO_2 nanoparticles was measured to be –63.96 mV and –44.40 mV in water and ethanol respectively, which is significantly higher than –48.06 mV and –37.87 mV for pure SiO_2 nanoparticles.

The suspensions of Fe_3O_4@SiO_2 showed apparent photonic colors at sufficiently high concentrations of the nanoparticles (**Figure 1**).[34] As shown in Figure 1a, the suspensions of Fe_3O_4@SiO_2 in acetonitrile showed the typical absorption colors of Fe_3O_4 in brown/dark grey when concentrations were lower than ~20 wt%. However, the suspension exhibited a strong photonic color in red at 30 wt%, and which gradually evolved to green as the concentration increased to 50 wt%. No significant change in color was observed at least for a month, when the containers were tightly sealed. The reflection spectra of the suspensions were very broad (FWHM = 130 ~ 150 nm) compared to other highly ordered photonic crystals (FWHM < ~50 nm).[9,12,35] Furthermore, as explored in detail below, their photonic colors were almost independent on the view angle while typical photonic crystals showed strong angle dependent hue.[36] These results suggest that the highly concentrated suspensions of Fe_3O_4@SiO_2 nanoparticles form quasi-amorphous PBG materials.[17–20]

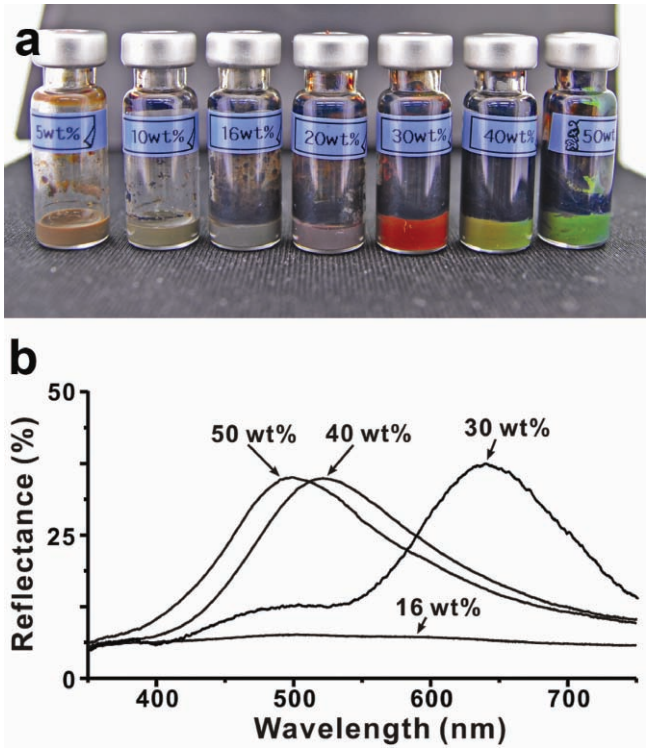

Figure 1. Concentration dependent photonic colors of Fe_3O_4@SiO_2 core-shell nanoparticles dispersed in acetonitrile. (a) Photograph of Fe_3O_4@SiO_2 suspensions with different concentrations (5 wt%–50 wt%). No photonic color is observed below 20 wt%. The suspensions exhibit photonic colors when the concentrations are higher than 30 wt%. (b) Reflection spectra of Fe_3O_4@SiO_2 suspensions at different concentrations (16 wt%, 30 wt%, 40 wt% and 50 wt%). The color varies to the shorter wavelength regime as increasing the concentration.[34]

The concentration dependent color changes of Fe_3O_4@SiO_2 suspensions in combination with their electrophoretic responses were used for fabricating the electrically tunable photonic display pixels. Our photonic display pixel consists of transparent top and bottom electrodes separated by 50 μm thick epoxy spacers (**Figure 2a**). Fe_3O_4@SiO_2 suspension (20–30 wt% in propylene carbonate) was injected in between those electrodes by using the conventional vacuum injection technique. Among many choices of solvents, propylene carbonate was selected for our electric tuning experiments due to its high electrochemical stability and low vapor pressure (3 Pa at 298.15 K).[37] When the concentration was optimized at 25 wt%, the photonic pixel was initially dark red to the eye without application of bias voltage. Due to their negative surface charge, Fe_3O_4@SiO_2 nanoparticles localized on the positive electrode upon application of bias voltage (Figure S2), and the resultant increase of the local concentration induced the changes of photonic color. Upon application of bias voltage, the photonic pixel with the size of 5 cm × 5 cm immediately exhibited uniform colors, and which were dependent on the bias voltage (Figure 2, Movie S1 & S2). For example, the photonic pixel was red (λ_{peak} = 655 nm) at 1.0 V, green (λ_{peak} = 536 nm) at 2.5 V and blue (λ_{peak} = 490 nm) at 4.0 V.[34] The color changes were fully reversible. When the bias voltage was removed, the pixel quickly returned to the original state. It is worth to mention that the color changes were only dependent on the applied voltage, but not on the cell current or operating time. For example, no significant color change was observed while the pixel continuously operated for 10 h at 2.5 V (**Figure 3a**). This feature suggests that the color changes were not driven by kinetic factors such as redox reactions but more likely by (pseudo-)thermodynamic equilibrium of colloidal particles in electric field. Our photonic pixel responded very fast to the change of the applied voltage. As shown in Figure 3b,c, the response time was measured to be 50 ms and 170 ms for on-switching (from 0 V to 4 V) and off-switching (from 4 V to 0 V) respectively. We expect that the response time can be further improved by using solvents with lower viscosity. Electrophoretic control of photonic color was also applicable to other colloidal nanoparticles. For example, pure SiO_2 nanoparticles suspensions also exhibited photonic colors in response to the applied electric field, but their optical contrast and tunability were very poor.

Due to the isotropic nature of quasi-amorphous structures, the photonic colors were almost independent of the view angle (Figure 4 and Figure S3). As shown in Figure 4a, the reflection spectra taken at several different angles (0–40°) for a photonic

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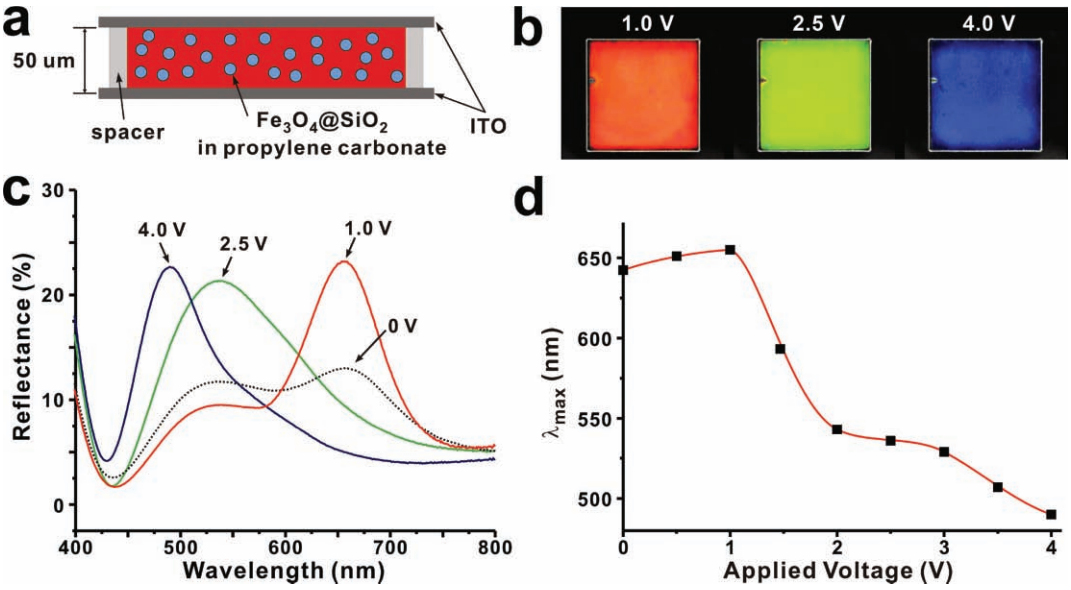

Figure 2. Tunability of photonic display pixel against the applied electric stimuli. (a) Schematic structure of photonic display pixel. The concentration of Fe_3O_4@SiO_2 is optimized at 25 wt% in propylene carbonate. (b) Photographs taken at 1.0 V, 2.5 V and 4.0 V of bias voltages. The pixel size is 5 cm × 5 cm. (c) Reflection spectra taken at increasing bias voltage.[34] (d) The change of photonic band position by 165 nm from 655 nm to 490 nm as a function of the applied voltage.

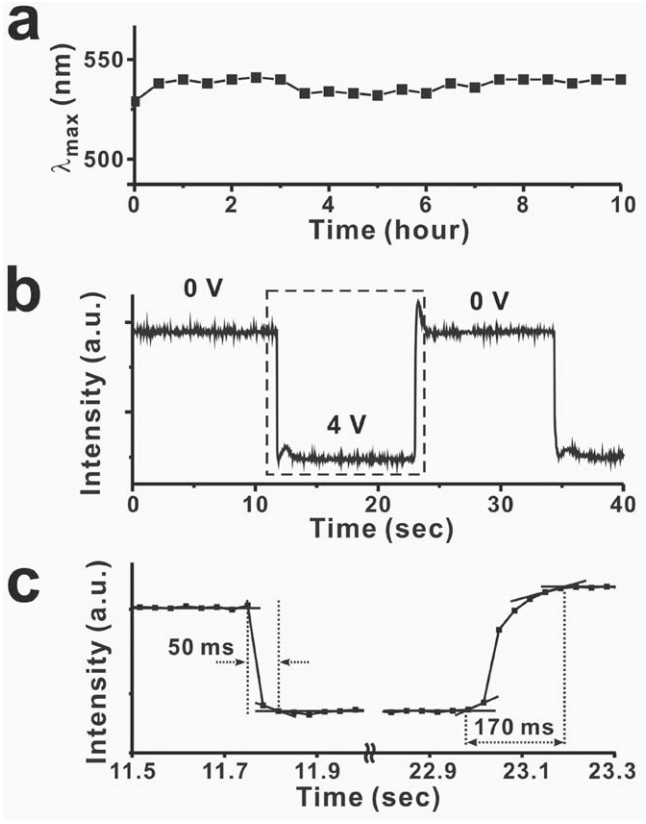

Figure 3. (a) The changes of photonic band position as function of operating time. No significant color change is observed during 10 h of continuous operation at 2.5 V. (b,c) Response time measurements of a photonic display pixel. The square region highlighted with dashed line on panel b is magnified on panel c.

pixel exhibiting a green color were almost identical. In this case, the spectral shifts were less than 5 nm. The same angle independency was also observed for the photonic pixel exhibiting a red color (Figure 4b). In contrast to the quasi-amorphous photonic pixels, the highly ordered 1D photonic crystals prepared by self-assembly block copolymers[9] showed a large spectral shift ($\Delta\lambda_{peak}$ = 83 nm) at the same experimental condition. Although the reflection spectra were taken in the range of 0–40° of detection angle due to the instrumental limitations, the angle independent feature was still effective in the wider range of detection angle (0–60°) (Figure S3). As compared in Figure S3, the colors of the quasi-amorphous photonic pixel looked almost same as the view angle changed from 0° to 60°, whilst those of the 1D photonic crystal film sharply varied from red to bluish green. Finally, we have demonstrated a flexible display pixel (Movie S3). The fluidic nature of our quasi-amorphous photonic materials was useful for fabricating the flexible and shaped devices.

In summary, electrically tunable display pixels exhibiting angle independent photonic colors across the visible region (490 to 655 nm) have been demonstrated using Fe_3O_4@SiO_2 quasi-amorphous colloidal structures. To our knowledge, this is the first demonstration of electrically tunable full color photonic display pixels based on quasi-amorphous colloidal structures. Ongoing work in our laboratory is improving the optical characteristics of photonic display pixels (reflectivity, color purity and etc.). We anticipate that our results provide useful information for understanding the optical properties of non-periodic photonic materials and suggest novel design rules for photonic devices. Especially, the features of our quasi-amorphous photonic pixel such as the angle-independent photonic color with high tunability, low driven voltages, fast response time, high stability and easy fabrication are promising for dynamic photonic displays.

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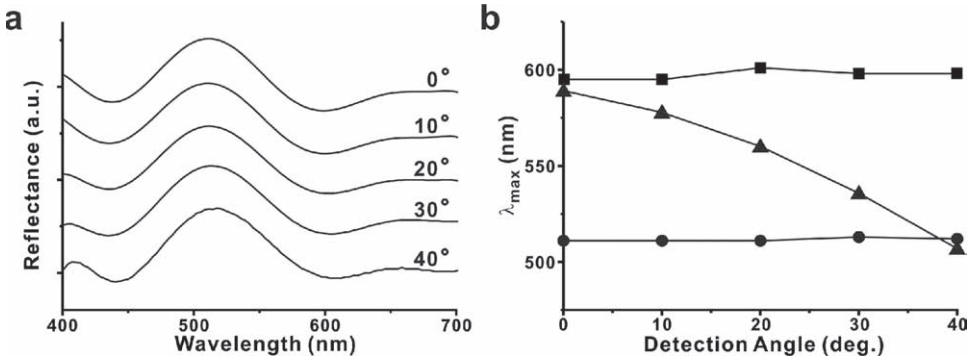

Figure 4. Angular independent optical responses of photonic display pixel. (a) Reflection spectra of a photonic display pixel exhibiting green color at 3 V. (b) The changes of photonic band position as function of detection angle. The optical responses of quasi-amorphous photonic pixels exhibiting green (•) or red (■) in color with variation of detection angle are well distinguished from those of 1D crystalline photonic crystals prepared by self-assembly of block copolymers (▲) (see also the Supporting Information for photographs taken at view angles from 0° to 60°).

Experimental Section

Materials and Instruments: Iron(III) chloride ($FeCl_3$, 97%), ammonium hydroxide (28 ~ 30%), diethylene glycol (99%), sodium hydroxide (NaOH, 97%), poly(acrylic acid) (PAA, M_w = 1800 g/mol), tetraethyl orthosilicate (TEOS, 98%), acetonitrile (99.5%) and propylene carbonate (99%) were purchased from Sigma-Aldrich Chemicals. Absolute ethyl alcohol was purchased from Fisher Scientific. Indium tin oxide (ITO) coated glasses with a resistivity of 7 Ω/cm were purchased from Corning Corp. Reflectance spectra were taken on Varian Cary 4000 or on Ocean Optics USB2000 spectrometer in reflection mode. Photographic images were taken under white fluorescent light using a digital camera (Nikon D-90). Scanning electron microscopy (SEM) images were taken on a Hitachi S-4800. Transmission electron microscopy (TEM) images were taken on JEOL JEM-2100F. An Agilent Technologies E3631A dc power supply was used to apply voltage to the photonic pixels.

Synthesis of $Fe_3O4@SiO_2$: $Fe_3O_4@SiO_2$ core-shell nanoparticles were synthesized according to previously reported procedures with some modifications.[30,31] Fe_3O_4 nanoparticle clusters were first synthesized by hydrolysis of iron(III) chloride in a basic condition at an elevated temperature (220 °C). Typically, a solution of NaOH (25 mmol) in diethylene glycol (10 mL) was heated at 120 °C for 1 h under nitrogen atmosphere, cooled, and kept at room temperature (Stock A). A mixture of $FeCl_3$ (0.4 mmol), PAA (8 mmol) and diethylene glycol (40 mL) was heated to 220 °C for 30 min under nitrogen atmosphere (Stock B). An aliquot of Stock A (4 mL) was quickly injected to Stock B, and the mixture was allowed to react further at 220 °C for 3 h. Fe_3O_4 nanoparticle clusters were collected by centrifugation and washed with deionized (DI) water and ethanol several times. SiO_2 shells were formed around the Fe_3O_4 nanoparticle clusters through sol-gel process using tetraethoxysilane (TEOS) as a precursor for SiO_2. For example, 50 mg of Fe_3O_4 nanoparticle clusters were dispersed in a mixture of DI water (6 mL) and ethanol (40 mL), and then a mixture of ammonium hydroxide (28%, 2 mL) and TEOS (0.2 mL) was slowly injected to the solution containing Fe_3O_4 nanoparticle clusters with a speed of 0.3 mL/h. Finally $Fe_3O_4@SiO_2$ core-shell nanoparticles were collected by magnetic separation, and washed with ample amount of ethanol. The purified $Fe_3O_4@SiO_2$ nanoparticles were redispersed into various solvents including water, methanol, ethanol, isopropyl alcohol, acetonitrile, dimethylformamide, dimethyl sulfoxide and propylene carbonate with the assistance of sonication.

Preparation of Devices: The photonic display pixel consists of transparent top and bottom electrodes separated by 50 μm thick epoxy spacers. $Fe_3O_4@SiO_2$ suspension (20–30 wt% in propylene carbonate) was injected in between those electrodes by using the conventional vacuum injection technique. The spacers were fabricated by using a dispenser machine (Eugene Tech.) and epoxy sealant (MATT AD-1066, EICT) containing 50 μm glass beads.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This research was supported by Research and Business Development Program (RBD-0802–3200-06–2) funded by the Korea Institute for Advancement of Technology (KIAT) affiliated with the Ministry of Knowledge Economy (MKE) of Korea.

Received: May, 27, 2010
Published online: August 23, 2010

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